

# PATENT SPECIFICATION

1,121,721

NO DRAWINGS.

Inventor:—GRANVILLE SHUTTLEWORTH.

Date of filing Complete Specification: 28 March, 1967.

Application Date: 30 March, 1966. No. 14175/66.

(Patent of Addition to No. 998,745 dated 4 May, 1964).

Complete Specification Published: 31 July, 1968.

© Crown Copyright 1968.



1,121,721

Index at Acceptance:—B5 A(1R14C1X, 1R55).

Int. Cl.:—B 29 d 9/00.

## COMPLETE SPECIFICATION.

### Improvements in or relating to Flooring Materials.

We, THE MARLEY TILE COMPANY LIMITED, a British Company, of London Road, Riverhead, Sevenoaks, Kent, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in or relating to flooring materials, especially flooring materials possessing antistatic or conductive properties. In particular, the invention is an improvement in or modification of the invention described and claimed in Specification No. 998,745.

Specification No. 998,745 describes and claims a method of manufacturing a vinyl chloride homopolymer or copolymer flooring material possessing antistatic or conductive properties which comprises preparing a granulate of a vinyl chloride homopolymer or copolymer, coating the granules of the said granulate with a conductive adhesive composition comprising a conductive powder together with a powdered, plasticised, thermoplastic resin, compressing the coated granulate into a sheet or slab and dividing the sheet or slab to form at least one lamina at least one surface of which consists essentially of the uncoated faces of split granules. The conductive adhesive composition used in the working Example of Specification No. 998,745 is a homogeneous mixture of polyvinyl chloride homopolymer ("Corvic" H 55/34—the word "Corvic" being a registered Trade Mark), a barium cadmium zinc stabiliser, conductive carbon black and dioctyl phthalate as plasticiser.

The present invention is based upon the discovery that a particularly advantageous conductive adhesive composition for use in the method described and claimed in

[Price 4s. 6d.]

Specification No. 998,745 takes the form of an aqueous vinyl chloride homopolymer or copolymer emulsion containing a conductive powder, and that such an emulsion can be replaced by other aqueous polymeric emulsions if so desired.

According to the present invention, there is thus provided a method of manufacturing a vinyl chloride homopolymer or copolymer flooring material possessing antistatic or conductive properties which comprises preparing a granulate of a vinyl chloride homopolymer or copolymer composition as herein defined, coating the granules of the said granulate with an aqueous polymeric emulsion containing a conductive powder, evaporating the water from the said aqueous polymeric emulsion, compressing the coated granulate into a sheet or slab and dividing the sheet or slab to form at least one lamina at least one surface of which consists essentially of the uncoated faces of split granules.

By the term "vinyl chloride homopolymer or copolymer composition" as used herein, we mean a composition comprising a vinyl chloride homopolymer or copolymer together with additives necessary to the formation of a satisfactory flooring material. The particular vinyl chloride homopolymers and copolymers and the particular additives desirably used, as well as the preferred proportions thereof incorporated into the composition, are as described in Specification No. 998,745. Also, the vinyl chloride homopolymer or copolymer composition is advantageously formed into a granulate by the method as described in Specification No. 998,745, the particle size of the granules being conveniently not greater than 0.75 inches and preferably within the range of from 0.06 to 0.375 inches.

The aqueous polymeric emulsions will in

general comprise a resin produced by emulsion polymerisation. Aqueous vinyl chloride homopolymer or copolymer emulsions (hereinafter referred to as polyvinyl chloride emulsions) are preferred; other emulsions which may be used include aqueous vinyl acetate homopolymer and copolymer emulsions, aqueous butadiene acrylonitrile polymeric emulsions, and acrylate and methacrylate polymeric emulsions.

The aqueous vinyl chloride homopolymer or copolymer emulsion, where used, comprises a colloidal dispersion of the resin in water. The resin particles will conveniently have an average particle size of from 0.1 to 1 microns, preferably about 0.25 microns. The resin is a vinyl chloride homopolymer or copolymer, for example a vinyl chloride/vinyl acetate or vinyl chloride/vinylidene chloride copolymer. A particularly convenient resin is that available under the trade name "Breon 151", the word "Breon" being a registered Trade Mark.

The aqueous polyvinyl chloride emulsion also conveniently contains a plasticiser, phthalate plasticisers being preferred. Examples of phthalate plasticisers which may be used include dinonyl, dioctyl,  $C_7-C_8$  alkyl and butylbenzyl phthalates. Phosphate plasticisers may also be employed e.g. tri-xylenyl and tri-tolyl phosphates. Other suitable plasticisers include low temperature plasticisers such as dioctyl sebacate and dioctyl adipate.

The polyvinyl chloride emulsion will also desirably contain a stabiliser, that is a substance capable of retarding decomposition of the resin during compounding and exposure to light. Mixtures of barium and cadmium salts of fatty acids such as for example stearic, lauric and ricinoleic acids, provide suitable stabilisers. Other substances which may with advantage be used include certain organo-tin compounds e.g. dibutyl tin dilaurate, and lead-containing compounds such as dibasic lead carbonate and lead stearate.

In order to ensure that a stable polyvinyl chloride emulsion is obtained, it is convenient also to incorporate an emulsifying agent which may for example be an alkyl aryl polyethylene glycol ether.

The emulsion advantageously also contains a thickening agent in a proportion selected to provide an emulsion of the desired consistency for application as a coating on to the granulate. Suitable thickening agents include for example sodium polyacrylate, alginates, caseinates or derivatives of cellulose.

The conductive powder is advantageously conductive carbon black or graphite. Conductive carbon black is a readily available substance and one suitable grade of conductive carbon black is that sold under the

proprietary trade name of "Vulcan XC/72", the word "Vulcan" being a registered Trade Mark. Where graphite is used, it preferably has a particle size in the range of from 100 B.S. mesh to 300 B.S. mesh, advantageously about 150 B.S. mesh. Other conductive powders which may be used include aluminium and copper powders.

The polyvinyl chloride emulsion, when used, preferably contains from 20 to 60% by weight of vinyl chloride homopolymer or copolymer. For every 100 parts by weight of resin, the emulsion preferably contains from 20 to 70 parts by weight of plasticiser; from 2 to 10 parts by weight of stabiliser; and from 0.5 to 3 parts by weight of emulsifying agents.

The proportion of conductive powder incorporated into the emulsion depends upon the degree of conductivity which is to be imparted to the flooring material. Thus, for example, if all that is desired is to render the flooring material suitable for use in the preparation of antistatic flooring, then a proportion of conductive carbon black or graphite up to 40 parts preferably from 10 to 40 parts and advantageously about 16 parts by weight per 100 parts by weight of the resin in the emulsion is generally adequate. If a flooring material suitable for use in the preparation of conductive flooring is required, however, a higher proportion of conductive carbon black or graphite up to, for instance, 70 parts (e.g. from 60 to 70 parts) by weight per 100 parts by weight of resin in the emulsion may be required.

The ingredients of the polyvinyl chloride emulsion conveniently include plasticiser, stabiliser, emulsifying agent and thickening agent as well as the conductive powder.

The emulsion coating may be provided on the granules in any convenient way. The proportion of emulsion used for the coating of course depends upon the conductive properties required of the flooring material, but a proportion of emulsion in the range of from 5 to 25% by weight based upon the weight of the granules is generally preferred, the conductivity being further controllable by variation of the amount of conductive powder in the emulsion.

After coating, the water present in the coating must be removed by evaporation. This may for example be achieved by heating the granules in an oven. Alternatively and preferably the granules are hot when coated with the emulsion whereby the water evaporates off in a short length of time.

After removal of the water, the coated granules are then consolidated into sheets or slabs, usually with the aid of heat, the preferred thickness of the slabs or sheets formed being dependent upon the ease of consolidation. Thus, it is difficult to consolidate slabs or sheets of a thickness greater than about

1" due to the problem of heating the granules throughout the thickness of the slabs or sheets during consolidation. Slabs or sheets up to about 1½" thick can however with difficulty be consolidated. The slabs or sheets are to be divided after consolidation, and the minimum thickness of slab or sheets is therefore governed by the problems of satisfactorily slicing these slabs or sheets. In general, slabs or sheets having a thickness in the range of from 0.5 to 1.5 ins., preferably 0.5 to 1 ins. and advantageously about 0.625 ins., are conveniently used.

The dividing of the slabs or sheets into laminae is suitably effected using a slicing machine, for example a slicing machine utilising a horizontal revolving knife. The thickness of the slices depends upon the thickness of flooring material required, and must be chosen to provide a flooring material of adequate thickness. Thus, acceptable flooring material should preferably have a thickness of at least 0.04 inches and, more commonly, at least 0.05 inches, and the minimum thickness of the laminae therefore is generally 0.04 inches. The maximum thickness is limited by economic considerations, and will not under normal circumstances be greater than 0.5 ins. It will be appreciated that the outside laminae obtained from a given slab or sheet are preferably not used as one of each of their surfaces does not consist essentially of uncoated faces of split granules. It is the laminae both surfaces of which are freshly produced by the dividing operation which are preferred and thus, it is preferable first to remove a relatively thin lamina from the slab or sheets, e.g. a lamina of about 0.02 inches, and then divide the remaining part of the slabs or sheets into laminae of the required thickness for flooring materials.

There is usually a certain unevenness in the surfaces of laminae produced by dividing slabs or sheets as described above. Thus, it is preferable to subject the laminae to a finishing operation to remove this unevenness. A suitable finishing operation comprises ironing out any unevenness using, for instance, a hot hydraulic press.

The following example, in which all parts are by weight, illustrates the invention:—

#### EXAMPLE

##### Composition of polyvinyl chloride granulate

|  | Parts |
|--|-------|
| Polyvinyl chloride homopolymer ("Breon 113", the word "Breon" being a registered Trade Mark) ... | 30    |
| Diocetyl phthalate ...   | 12    |
| Barium cadmium zinc liquid stabiliser (Lankro Mark KCB) ...                                      | 2     |
| Titanium dioxide ...   | 5     |
| Ground whiting ...   | 51    |

#### Preparation of granulate

The above ingredients are compounded in a Shaw intermixer (the word "Shaw" being a registered Trade Mark) at 160°C under pressure to fuse and consolidate. The composition thus formed is made into sheet form by passing through a sheeting mill at temperatures of 155°C (hotter side of mill) and 145°C (cooler side of mill), the sheets thereby produced having a thickness of 0.31 ins. These sheets are next fed into a Masson-Scott granulator of the shear knife type to produce a granulate the granules of which all pass a 0.31 ins. mesh sieve.

#### Conductive composition

A conductive composition is prepared by mixing a dispersion of carbon black and an emulsion of plasticiser and stabiliser with a polyvinyl chloride emulsion in the following proportions:—

|   | Parts by Weight |
|---|-----------------|
| Carbon black dispersion ...               | 40              |
| Plastiser-stabiliser emulsion ...         | 25              |
| Breon 151 polyvinyl chloride emulsion ... | 100             |

The plasticiser-stabiliser emulsion is stirred into the polyvinyl chloride emulsion and the carbon black dispersion added.

The carbon black dispersion is first prepared as follows:—

|   | Parts by Weight |
|---|-----------------|
| Carbon black ("Corax" L, the word "Corax" being a registered Trade Mark) ...              | 20              |
| "Belloid" TD (polyacryl sulphonate, the word "Belloid" being a registered Trade Mark) ... | 2               |
| Water ...   | 78              |

The water containing the dissolved Belloid TD dispersing agent is stirred vigorously and the carbon black added in small increments, the rate of addition being controlled by the rate of wetting out and dispersion of the pigment.

The emulsion of plasticiser and stabiliser is prepared as follows:—

|   | Parts by Weight |
|---|-----------------|
| Diocetyl phthalate ...  | 65              |
| Atlas G 1690 (alkyl acrylpolyethylene glycol ether, the word "Atlas" being a registered Trade Mark) ... | 0.6             |
| Barium cadmium zinc stabiliser (Lankro Mark KCB) ...  | 5               |
| Water ...   | 29.4            |

The emulsifier and stabiliser are dissolved in the diocetyl phthalate and water is added with vigorous agitation with a high speed

stirrer. The resulting emulsion is then passed through a colloid mill to give a fine particle size, stable emulsion.

*Preparation of flooring material from granules and conductive composition*

The granules (100 parts) are heated with hot air in a tumbler blender and 10 parts of the conductive coating are sprayed on to the granules to give a complete covering of the chips. Heating of the chips is continued until all water has been removed from the conductive composition coating.

60 lbs. of the coated granules are then consolidated in a hydraulic press, the plates of which are at 140°C to give a slab of material 0.580 ins. thick. A 0.020 ins. thickness is sliced off from the top of the slab using a slicing machine which utilises a horizontal rotating band knife. The remaining part of the slab is sliced into six portions each of 0.090 ins. thickness. These portions are repressed to iron out any unevenness in their surfaces and are subsequently cut into tile form.

WHAT WE CLAIM IS:—

1. A method of manufacturing a vinyl chloride homopolymer or copolymer flooring material possessing antistatic or conductive properties which comprises preparing a granulate of a vinyl chloride homopolymer or copolymer composition as herein defined, coating the granules of the said granulate with an aqueous polymeric emulsion containing a conductive powder, evaporating the water from the said aqueous polymeric emulsion, compressing the coated granulate into a sheet or slab and dividing the sheet or slab to form at least one lamina at least one surface of which consists essentially of the uncoated faces of split granules.

2. A method as claimed in claim 1 in which the said sheet or slab is divided to produce laminae both surfaces of which consist essentially of the uncoated faces of split granules.

3. A method as claimed in either of claims 1 and 2 in which the said granulate of the vinyl chloride homopolymer or copolymer composition comprises granules of average particle size from 0.06 to 0.375 ins.

4. A method as claimed in any of the preceding claims in which the said aqueous polymeric emulsion contains vinyl chloride homopolymer or copolymer resin.

5. A method as claimed in claim 4 in which the said emulsion contains vinyl chloride homopolymer or a vinyl chloride/vinyl acetate or vinyl chloride/vinylidene chloride copolymer.

6. A method as claimed in either of claims 4 and 5 in which the vinyl chloride homopolymer or copolymer resin has an average particle size of from 0.1 to 1 micron.

7. A method as claimed in claim 6 in which the said average particle size is about 0.25 microns.

8. A method as claimed in any of claims 4 to 7 in which the aqueous polymeric emulsion contains from 20 to 60% by weight of vinyl chloride homopolymer or copolymer.

9. A method as claimed in any of claims 4 to 8 in which the aqueous polymeric emulsion contains a phthalate or phosphate plasticiser.

10. A method as claimed in claim 9 in which the said emulsion contains from 20 to 70 parts by weight of plasticiser per 100 parts by weight of resin.

11. A method as claimed in any of claims 4 to 10 in which the said emulsion contains a stabiliser which is a mixture of barium and cadmium salts of a fatty acid, an organotin compound or a lead-containing compound.

12. A method as claimed in claim 11 in which the said emulsion contains from 2 to 10 parts by weight of stabiliser per 100 parts by weight of resin.

13. A method as claimed in any of claims 4 to 12 in which the aqueous polymeric emulsion contains an emulsifying agent.

14. A method as claimed in claim 13 in which the emulsifying agent comprises an alkyl aryl polyethylene glycol ether.

15. A method as claimed in either of claims 13 and 14 in which the said emulsion contains from 0.5 to 3 parts by weight of emulsifying agent per 100 parts by weight of resin.

16. A method as claimed in any of the preceding claims in which the aqueous polymeric emulsion contains a thickening agent.

17. A method as claimed in any of the preceding claims in which the aqueous polymeric emulsion contains carbon black or graphite as conductive powder.

18. A method as claimed in claim 17 in which the conductive powder is graphite having a particle size between 100 and 300 B.S. mesh size.

19. A method as claimed in any of claims 1 to 16 in which the aqueous polymeric emulsion contains aluminium or copper as conductive powder.

20. A method as claimed in either of claims 17 and 18 for the manufacture of a flooring material possessing antistatic properties in which the said emulsion contains up to 40 parts by weight of carbon black or graphite per 100 parts by weight of resin.

21. A method as claimed in claim 20 in which the said emulsion contains from 10 to 40 parts by weight of carbon black or graphite per 100 parts by weight of resin.

22. A method as claimed in either of claims 17 and 18 for the manufacture of a flooring material possessing conductive pro-

perties in which the said emulsion contains up to 70 parts by weight of carbon black or graphite per 100 parts by weight of resin.

5 23. A method as claimed in claim 22 in which the said emulsion contains from 60 to 70 parts by weight of carbon black or graphite per 100 parts by weight of resin.

10 24. A method as claimed in any of the preceding claims in which the proportion of aqueous polymeric emulsion applied as a coating to the granules is in the range of from 5 to 25% by weight based upon the weight of the granules.

15 25. A method as claimed in any of the preceding claims in which the coated granules are compressed into a sheet or slab having a thickness in the range of from 0.5 to 1.5 inches.

20 26. A method as claimed in claim 25 in which the coated granules are compressed into a sheet or slab having a thickness of from 0.5 to 1.0 inches.

27. A method as claimed in any of the preceding claims in which the sheet or slab

is divided to form at least one lamina having a thickness of at least 0.04 inches. 25

28. A method as claimed in claim 27 in which the sheet or slab is divided to form at least one lamina having a thickness of at least 0.05 inches. 30

29. A method as claimed in claim 27 in which the sheet or slab is divided to form at least one lamina having a thickness between 0.04 and 0.5 inches.

30. A method as claimed in claim 1 substantially as herein described. 35

31. A method as claimed in claim 1 substantially as herein described in the Example.

32. Polyvinyl chloride homopolymer or copolymer flooring material when manufactured by a method as claimed in any of the preceding claims. 40

For the Applicants,  
FRANK B. DEHN & CO.,  
Chartered Patent Agents,  
Imperial House,

15—19 Kingsway, London, W.C.2.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1968.  
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,  
from which copies may be obtained.